Journal of Chromatography, 214 (1981) 118–121
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,946

Note

Sample transfer in splitless injections in capillary gas chromatography

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(Received April 30th, 1981)

Splitless injections[1–4] are carried out using a split injector with a closed split exit during the sampling period, the "splitless period". During the splitless period, more than 95% of the sample is supposed to be transferred into the capillary column. The transfer is not complete because during the transfer of the vapour there are diffusion processes that continuously dilute the vapour with carrier gas. Further, there are corners in the injector system from which the sample reaches the column by diffusion processes rather than by a straight transfer. However, residual vapour in the injector is undesirable as it causes peak tailing, especially for the solvent peak, which becomes extremely broad. The splitless injection technique avoids this problem by purging the injector through the split exit line after a nearly complete sample transfer.

Thus, on the one hand the splitless period has to be sufficiently long to assure that most of the sample enters the column, but on the other hand the split valve has to be reopened early enough to avoid too broad a solvent peak.

The time required to obtain an acceptably complete transfer of the sample from the injector into the capillary may easily be determined by a series of injections with increasing length of the splitless period.

We considered a more basic study of the conditions and time involved in the sample transfer to be useful. A splitless injection requires a minimal carrier gas flow-rate, otherwise a sample transfer of 95% cannot be achieved with the normal injectors and sample volumes. Further, small-bore columns and "slow" carrier gases such as helium and nitrogen cause problems.

The required length of the splitless period depends on the carrier gas flow-rate and on geometrical factors such as the design of the injector and where the sample is released within the vaporizing chamber. The geometrical aspects have been discussed previously[5,6], the essential points being a sufficient volume to house the sample vapour and measures to minimize the dilution of the sample with carrier gas.

LENGTH OF THE SPLITLESS PERIOD

The experiments reported below were carried out on injectors from Carlo Erba (Milan, Italy), Models 2900 and 4160, corresponding to the injector described in ref. 2. The glass insert had an I.D. of 3.6 mm and a length of 80 mm and the capillary entered 8 mm into this liner. The syringe had a 7.5-cm needle and reached to within 15 mm of the capillary end. The septum purge was left open during the injections (5 ml/min). Repeated checks showed that no sample was lost through this line.

0021-9673/81/0000–0000/S02.50

The amount of sample transferred to the column was determined by injections of *n*-docosane (*n*-C_{22}), diluted 1:50,000 in *n*-hexane. The sample volume was 2 μl (1 μl reading on the syringe and 1 μl contained in the needle). Injections were carried out by the "hot needle" method[6], the injector being at 250°C. The peak area for 100% transfer of *n*-C_{22} to the column was determined (a) by splitless injections at a carrier gas flow-rate of 6 ml/min applying a splitless period of 3 min and (b) by cold on-column injections of the same sample volume using the same detector as for the splitless injections.

Fig. 1 shows the dependence of the amount of sample transferred on the carrier gas flow-rate and on the length of the splitless period. The column temperature during the injection was kept at 160°C to avoid recondensation of the solvent on the column. The *n*-C_{22} was eluted from a 22 m × 0.29 mm I.D. capillary column coated with 0.15 μm of SE-52 isothermally between 190 and 220°C (depending on the carrier gas flow-rate chosen). Little more than half of the sample was transferred during a splitless period of 3 min when the carrier gas flow-rate was at 0.5 ml/min, and it appears to be impossible to obtain a satisfactory transfer of the sample at this flow-rate even with a greatly prolonged splitless period. At 1 ml/min about half of the sample entered within only 40 sec, but the transfer was still only 75% complete after 3 min. A carrier gas flow-rate of 2 ml/min allowed a sample transfer of better than 95% within 1.5 min and 4 ml/min within less than 40 sec.

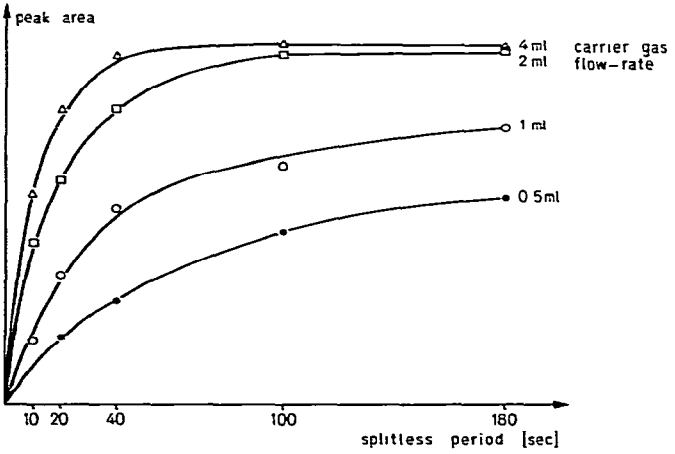


Fig. 1. Dependence of the amount of sample transferred on the duration of the splitless period for various carrier gas flow-rates. At 4 ml/min the transfer is better than 95% after about 40 sec; a (pre-set) carrier gas flow-rate of 2 ml/min requires a splitless period of 100 sec. Lower flow-rates do not allow a sample transfer within a reasonable period of time, especially being a problem for narrow-bore columns and "slow" carrier gases such as helium or nitrogen.

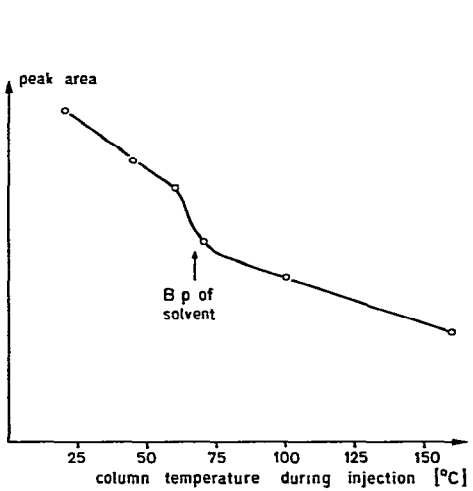
The results in Fig. 1 show that the transfer of the sample rapidly becomes difficult with decreasing carrier gas flow-rates. A halved carrier gas flow-rate more than doubles the transfer time because during the longer time involved the sample vapour is diluted. Eventually, with a decreasing flow-rate, dilution becomes more effective than sample transfer. Prolongation of the splitless period does not produce a sastisfactory result.

Under the conditions used (which correspond to those on many commonly

used injectors and which may be optimistic for others), the minimal carrier gas flow-rate to provide a 95% sample transfer is of the order of 2–3 ml/min with a splitless period of about 1.5 min.

The time required for the sample transfer may be considerably reduced by keeping the column temperature sufficiently low to promote recondensation of the solvent (*e.g.*, temperature conditions used for a solvent effect[2]). Recondensation of the vapour in the column inlet increases the flow-rate into the column and consequently reduces dilution of the sample vapour with carrier gas. Both processes make the sample transfer more efficient.

Fig. 2 shows the amounts of sample transferred into a column kept at different temperatures during a splitless period of 10 sec. The (pre-set) carrier gas hydrogen flow-rate was 1.5 ml/min. At 25°C more than 70% of the sample entered the column within the 10 sec (this proportion reached the column only after 2 min when at 100°C). The amount of sample transferred decreases with increasing column temperature, for the 10-sec period being halved at about 90°C (compared with 25°C) and becoming a third at 160°C.



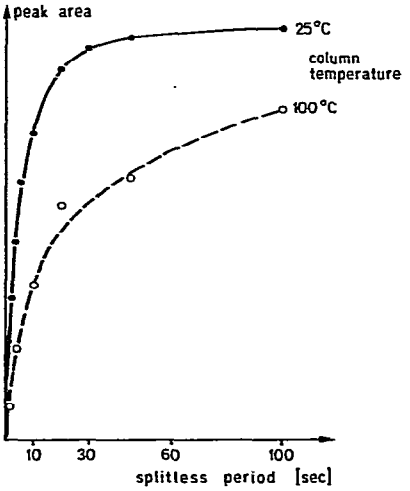


Fig. 2. Influence of column temperature on the speed of sample transfer: 2 μl of n-C_{22} diluted 1:50,000 in n-hexane; splitless period, 10 sec; pre-set carrier gas (hydrogen) flow-rate, 1.5 ml/min. Recondensation of the solvent in the column may increase the flow-rate into the capillary considerably.

Fig. 3. Amounts of sample entering the column at 25 and 100°C for different durations of the splitless period: 2 μl of n-C_{22} diluted 1:50,000 in n-hexane. At low column temperatures, promoting the recondensation of the solvent in the column, the sample is transferred more rapidly. At the (pre-set) carrier gas flow-rate chosen (1.5 ml/min), the column temperature was the deciding factor for the feasibility of an acceptably complete sample transfer.

Fig. 3 shows a comparison of the amount of sample entering the column at 25 and 100°C for different durations of the splitless period. During the first 1 sec, three times more material reaches the column at 25°C than at 100°C. After 3 sec the difference is lowered to a factor of 2. However, under the conditions chosen (pre-set carrier gas flow-rate 1.5 ml/min) the column temperature was the most important parameter for the feasibility of splitless injection. At a column temperature of 25°C the sample transfer was better than 95% after 45 sec; at 100°C a reasonably complete transfer was impossible.

DISCUSSION

The term "splitless injection" implies 95% or better sample transfer from the injector to the column. This is not only a matter of definition. If the sample is only partially transferred, different sample components may be "split" by different ratios, thus creating discrimination. In practical applications such discrimination may result from different diffusion speeds (discriminating the volatiles), adsorption on the glass liner, on dirty spots in the injector or on septum particles, or by degradation of labile components due to the extended residence time in the injector. The effects of adsorption or condensation in the injector may be reduced by a prolonged splitless period, which allows a several-fold transfer of the injector volume.

The experimental results show that a splitless injection requires a pre-set carrier gas flow-rate of at least 2 ml/min. Other important conditions involved are a sample volume of 1–2 μl, which in turn requires an injector volume of about 1 ml.

A carrier gas flow-rate of 2 ml/min is close to the flow-rate yielding optimal resolution on a capillary with an I.D. of 0.30 mm if hydrogen is used as the carrier gas. As such columns are commonly used with carrier gas flow-rates between 2 and 5 ml/min, this system is appropriate for splitless injections.

If the same 0.30-mm I.D. capillary is used with helium as the carrier gas, the flow-rate required for a similar resolution to that obtained with hydrogen is about half. Thus, a flow-rate of 2 ml/min, as required for splitless injection, is still practicable but it forces one to use the capillary under non-optimized conditions. With nitrogen as the carrier gas, requiring a three times slower flow-rate than hydrogen for optimal resolution, splitless injection approaches impracticality.

Capillary columns of I.D. 0.20–0.25 mm are designed to produce high efficiency, but their small size renders their usefulness for trace analyses questionable. If hydrogen is used as the carrier gas (as we recommend for a number of reasons[7]), a column of 0.25-mm I.D. may still be used reasonably at a carrier gas flow-rate of 2 ml/min. For helium or nitrogen, however, such flow-rates lower the efficiency of the columns by more than was gained by the reduction of the inner diameter of the column. Thus the apparently high efficiency of the column is not used in practice. Recondensation of the solvent in the column inlet may be used to reduce the duration of the splitless period. This technique makes splitless injection feasible for very low carrier gas flow-rates (1.5–2.5 ml/min).

Within limitations, it is possible to increase the carrier gas flow-rate during the injection to promote the sample transfer.

ACKNOWLEDGEMENT

We thank Professor R. Bromund for reading the manuscript.

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